Heat Contents and Heats of Fusion of III-V Compounds

R. H. COX[1] and M. J. POOL
University of Denver, Denver, Colo.

Heat contents have been measured over the temperature range 300° to 1200° K. for InSb, InAs, InP, GaSb, GaAs, GaP, AlSb, and AlP using a diphenyl ether drop calorimeter. Heat capacities were derived for all of the compounds and heats of fusion of 9.2, 5.6, and 8.0 kcal. per gram-atom were determined for InAs, InSb, and GaSb.

A GREAT deal of interest has developed in the III-V compounds since it was discovered that they are semiconductors. Although much has been published concerning their electronic properties, there has been very little work done on the thermodynamics of these compounds. An experimental determination of heat capacities and heats of fusion is particularly important since these data are often required in other thermodynamic calculations.

EXPERIMENTAL

Diphenyl Ether Calorimeter. A Bunsen-type, diphenyl ether calorimeter similar to those described by Jessup (*3*) and Hultgren *et al.* (*2*) was used in this study. The operation of the calorimeter is a simple procedure, and the heat content of the sample is measured in the following way.

The encapsulated sample is held for 20 minutes in an evacuated drop chamber which is centered in the tube furnace. Preliminary experiments demonstrated that after 15 minutes holding time, the samples attain equilibrium and the data are independent of time at temperature. The temperature is measured by a platinum-platinum–10% rhodium thermocouple located in a stainless steel block adjacent to the specimen. At the end of this time, the specimen is dropped from the furnace through a spring-loaded radiation gate. The specimen falls into a copper screen basket inside the calorimeter well. This basket breaks the fall of the sample and, together with the copper fins soldered to the copper well, facilitates heat transfer to the mantle of solid diphenyl ether frozen to the well and fins. Immediately after the drop, one atmosphere of argon is added to speed heat transfer from the specimen to the calorimeter well. Since both the solid and liquid diphenyl ether are maintained at the melting point throughout the run, essentially all of the heat contained in the specimen is used to melt a portion of the solid mantle. The expansion which accompanies this melting forces part of the mercury contained in a pool in the bottom of the calorimeter out through a tube into a horizontal length of calibrated capillary tubing. The heat content of the sample is calculated from the capillary measurements and is referenced to 300° K., the melting point of diphenyl ether.

Materials. All compounds used in this study were semiconductor grade and were the highest purity commercially available (>99.99%). The compounds were crushed and placed in spherical capsules formed from 4-mil tantalum foil. These capsules were then placed between two deep-drawn tantalum cups of the same thickness; the cups were heliarc welded shut and formed into 0.320-inch diameter capsules. This arrangement inhibited the decomposition of the high vapor pressure compounds and also served to contain the molten compounds. The weights of the capsules were routinely checked after each drop; any loss in weight indicated a failure, and the capsule was then discarded.

RESULTS AND DISCUSSION

Heat Capacity. Tantalum was used for calibration not only because it was the container material but its well-known heat content (*4*) made possible an estimate of radiant heat loss during the free-fall period. The heat content data were plotted as a function of the absolute temperature. A computer was used to fit the best curve to the data with the condition that $H_T - H_{300} = 0$ at $T = 300°$ K. The tantalum data were lower than the accepted data (*4*); the degree of deviation, which is a function of temperature, had a maximum value of 5% at the highest temperature. The low values, apparently, were a result of heat losses during the time the specimen was falling from the furnace into the calorimeter. An average correction factor was determined from these data using the computer, and this factor was applied to the data for all of the compounds. Since the conditions were essentially the same for all drops from any one temperature, the use of an average correction factor is valid. The three arbitrary constants in the expression

$$H_T - H_{300} = A + BT + CT^2$$

were obtained from a least squares fit of the data for the solid compounds and the standard deviations were obtained. Only the GaAs and InAs data required the quadratic term. The data from the other compounds and from the liquids were fit to a linear expression. The heat capacity equations were obtained by differentiation of the heat content expressions (Table I). The reproducibility of the measurements is given by the standard deviations. The accuracy of the measurements depends upon how well one can measure the change in length of the mercury column of the calorimeter. Since the exactness in reading the column is fixed, the accuracy of the data increases at higher temperatures where the larger amount of heat given up (for the same sample weight) produces a larger change in column length. For this system, the following accuracies were valid: at 400° K., ± 2%; at 800° K., ± 0.4%; and at 1300° K., ± 0.2%.

There is only a limited amount of experimental high temperature heat capacity data published in the literature. Nachtrieb and Clement (*7*) reported for InSb the following values: $C_p(293 - 363°\text{K.}) = 6.15$, $C_p(363 - 443°\text{K.}) = 6.63$, $C_p(443 - 623°\text{K.}) = 7.34$, and $C_p(623 - 773°\text{K.}) = 7.34$ cal. per gram-atom °K. Schneider and Blachnik (*9*) gave the following heat capacities for InSb: $C_p(383 - 583°\text{K.}) = 5.85$, $C_p(583 - 803°\text{K.}) = 6.50$, and $C_p(803 - 933°\text{K.}) = 7.4$ cal. per gram-atom °K. Kochetkova and

---

[1] Present address: Texas Instruments Inc., Dallas, Tex.

Table I. Heat Content and Heat Capacity Equations for the III-V Compounds

Compound	$H_T - H_{298}$, Cal./Gram-Atom	Standard Deviation, Cal./Gram-Atom	Temperature Range, ° K.	C_p, Cal./Gram-Atom, ° K.
InSb(s)	$-1847 + 6.19T$	210	298–798	6.2
InSb(l)	$3486 + 6.5T$	228	798–1100	6.5
InAs	$-1631 + 5.32T + 5.20 \times 10^{-4}T^2$	133	298–1200	$5.3 + 1.0 \times 10^{-3}T$
InP	$-1839 + 6.17T$	188	298–1200	6.2
GaSb	$-1869 + 6.27T$	209	298–985	6.3
GaAs	$-1645 + 5.41T + 3.64 \times 10^{-4}T^2$	100	298–1250	$5.4 + 7.3 \times 10^{-4}T$
GaP	$-1699 + 5.70T$	437	298–1200	5.7
AlSb	$-1904 + 6.39T$	184	298–1150	6.4
AlP	$-1762 + 5.91T$	179	298–1150	5.9

Rezukhina (*5*) measured the heat capacity of GaSb over the temperature range 293° to 993° K. Their resultant heat capacity was $5.656 + 1.521 \times 10^{-3}\,T$ cal. per gram-atom ° K.

Piesbergen's (*8*) data yields the following heat capacities at 298° K.: C_p(InSb) = 5.91, C_p(InAs) = 5.71, C_p(InP) = 5.43, C_p(GaSb) = 5.80, C_p(GaAs) = 5.53, and C_p(AlSb) = 5.54 cal. per gram-atom ° K. Gultyaev and Petrov (*1*) reported 5.88 cal. per gram-atom ° K. at 300° K. for InSb. Musgrave (*6*) calculated a value of 5.9 cal. per gram-atom ° K. for InSb at 400° K.

The high vapor pressure over the compounds limited the upper temperature range at which the heat content could be investigated. All the compounds were sealed in welded tantalum capsules, thus retarding vaporization, but a tiny leak developed occasionally, and the capsule then had to be discarded. A clearly defined heat content curve was obtained for liquid InSb, and the heat capacity of 6.5 cal. per gram-atom ° K. is a reasonable value, being slightly larger than that of the solid. Fewer data points were obtained for liquid GaSb and InAs because capsule lifetime was shortened by the apparent reaction of the compounds with the tantalum. These data were not sufficiently accurate at temperatures beyond the melting point to determine the heat capacities of the liquid.

Heat of Fusion. The heats of fusion in kcal. per gram-atom for InSb (5.6), GaSb (8.0), and InAs (9.2) were obtained from the discontinuity in heat content upon extrapolating the curves for both phases to the melting temperature. The following melting temperatures were used: InSb = 798° K., GaSb = 985° K., and InAs = 1213° K. The value for InSb is slightly lower than the value of 5.9 kcal. per gram-atom given by Schneider and Blachnik (*9*), the value of 6.1 found by Schottky and Bever (*10*), and the value of 5.8 found by Terpilowski and Trzebiatowski (*11*). The value for GaSb is 2 kcal. per gram-atom higher than that given by Schottky and Bever (*10*); and the value for InAs is 3 kcal. per gram-atom higher than Vieland's (*12*) estimate.

The accuracy of the heats of fusion depends upon the reliability of the heat content curves for the liquids. The heat content data for InSb in the liquid state were clearly defined, but the data for liquid GaSb and InAs were less accurate. Therefore, the heat capacity for the liquid was assumed to be equal to that of the solid in order to determine the heat of fusion for GaSb and InAs. The accuracy of the heat of fusion data increases in the order of InSb > GaSb > InAs. The probable errors in the measurements are ± 4% for InSb and ~ ± 10% for GaSb and InAs.

ACKNOWLEDGMENT

The authors acknowledge the assistance of Hugh Warren and Dale Prine in carrying out the experimental work. Appreciation is extended to Eric Jones for the computer work and to Hans Strack for his helpful comments.

LITERATURE CITED

(1) Gultyaev, P.V., Petrov, A.V., *Soviet Phys.-Solid State (English Transl.)* 1, 330–4 (1959).
(2) Hultgren, R., Newcombe, P., Orr, R.L., Warner, L., *Natl. Phys. Lab. Gt. Brit. Proc. Symp.* No. **19**, 1, 118 (1960).
(3) Jessup, R.S., *J. Research Natl. Bur. Standards* **55**, No. 6, 222–7 (1955).
(4) Kelly, K.K., King, E.G., *U. S. Bur. Mines Bull.* No. **592** (1961).
(5) Kochetkova, N.M., Rezukhina, T.N., *Vopr. Met. i Fiz. Poluprov., Akad. Nauk S.S.S.R. Tr. 4-go Soveshch., Moscow* **1961**.
(6) Musgrave, M.J.P., *Phys. Rev. Letters* **5**, 97 (1963).
(7) Nachtrieb, N.H., Clement, N., *J. Phys. Chem.* **62**, 876 (1958).
(8) Piesbergen, U., *Z. Naturforsch.* **18a**, 141–7 (1963).
(9) Schneider, A., Blachnik, R., *Naturwissenschaften* **20**, 465–6 (1962).
(10) Schottky, W.F., Bever, M.B., *Acta Met.* **6**, 320–6 (1958).
(11) Terpilowski, J., Trzebiatowski, W., *Bull. acad. polon. sci., Sér. sci. chim.* **8**, 95–8 (1960).
(12) Vieland, L.J., *Acta Met.* **11**, 137–42 (1963).

Received for review February 21, 1966. Accepted December 6, 1966. Financial assistance for this work was provided by the Air Force Cambridge Research Laboratories under Contract No. AF 19(604)-7222. This work was part of a thesis submitted to the University of Denver by R. H. Cox in partial fulfillment for the degree of Doctor of Philosophy.